Synthesis of an Unusual, High Nuclearity Osmium–Platinum Cluster: *X*-Ray Analysis of $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (C_8H_{12} = cyclo-octa-1,5-diene)

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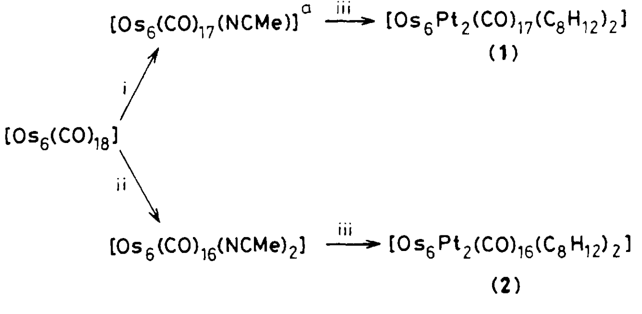
Reaction of $[Os_6(CO)_{18-n}(NCMe)_n]$, $n = 1$ or 2, with $[Pt(C_8H_{12})_2]$ (C_8H_{12} = cyclo-octa-1,5-diene) results in formation $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$ (**1**) and $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (**2**), respectively, and (**2**) has been shown by X-ray analysis to possess the unusual metal core geometry of two edge-fused Os tetrahedra, one of which is Pt-bicapped.

Mixed metal cluster complexes have been synthesized by a number of general routes including pyrolyses, addition to co-ordinatively unsaturated clusters, redox condensations, and reaction of carbonylmetallates with metal halides.[1] We have recently reported[2] the preparation of $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$ (C_8H_{12} = cyclo-octa-1,5-diene) (**1**) from the treatment of a toluene–acetonitrile solution of $[Os_6(CO)_{20}]$[3] with $[Pt(C_8H_{12})_2]$.[4] It has since been demonstrated[5] that this reaction proceeds *via* the cluster $[Os_6(CO)_{19}(NCMe)_2]$[6] which combines with $[Pt(C_8H_{12})_2]$ to yield (**1**). Thus the mixed metal cluster forms by the reaction of a cluster and a complex which both contain weakly bound ligands. We have extended this method and now report the synthesis of (**1**) and the unusual cluster $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (**2**) by reaction of $[Pt(C_8H_{12})_2]$ with $[Os_6(CO)_{18-n}(NCMe)_n]$,[7] where $n = 1$ or 2, respectively. The cluster (**2**) has a metal core geometry which cannot be explained by conventional skeletal electron counting procedures[8] or by the condensed polyhedra approach.[9]

The synthesis of (**1**) and (**2**) from $[Os_6(CO)_{18}]$ is summarized in Scheme 1. The crystal structure of (**1**) has been previously reported[2] and the metal core geometry may be described as a regular octahedron of osmium atoms with two face-capping $Pt(C_8H_{12})$ units. In terms of overall electron counting (**1**) is a 110-electron system and the observed structure is in agreement with that proposed by skeletal electron counting methods.[8] The cluster core geometry is the same as that found for the isoelectronic osmium anion[10] $[Os_8(CO)_{22}]^{2-}$

Dark brown crystals of (**2**) suitable for *X*-ray analysis† were obtained by slow evaporation of an ethyl acetate solution. A perspective view of the cluster is presented in Figure 1. The molecule possesses a crystallographically imposed 2-fold axis bisecting the Os(3)–Os(3′), Os(1)–Os(1′), and Os(2)–Os(2′) edges. There are 16 carbonyl ligands all of which are linear and terminally bound to the Os atoms, and two cyclo-octa-1,5-diene ligands each chelating to a Pt atom. The metal core geometry may be regarded as a Pt-bicapped Os-tetrahedron which is linked to a second Os-tetrahedron through a common edge, Os(1)–Os(1′).



Scheme 1. i, slow addition of 1 equiv. of Me_3NO, ($MeCN–CH_2Cl_2$); ii, 2 equiv. of Me_3NO; iii, $[Pt(C_8H_{12})_2]$, CH_2Cl_2, reflux for 15 min. All the reactions were performed under an N_2 atmosphere. The products were purified using silica gel t.l.c. plates (4 : 1 hexane–CH_2Cl_2 eluant). (**2**) I.r. (CH_2Cl_2) (ν_{CO}), 2075 (m), 2057 (vs), 2032 (m,sh), 2017 (s), 2009 (s), 1988 (s), and 1960 (w) cm^{-1}. [a] See ref. 7.

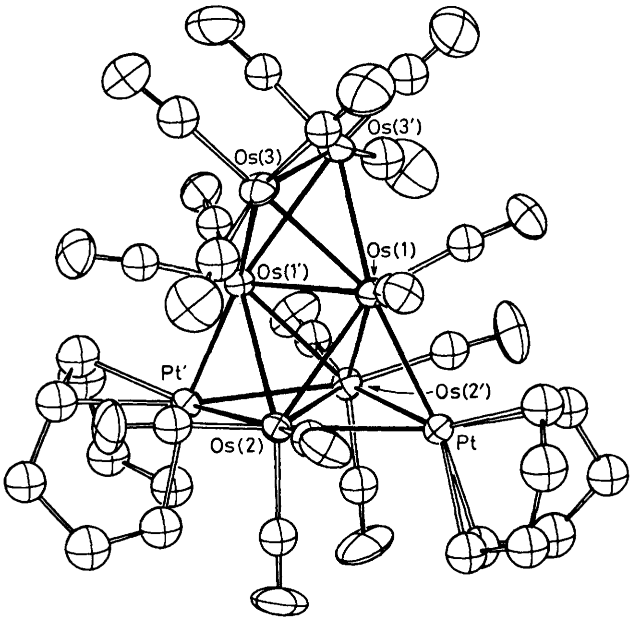


Figure 1. The structure of $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ (**2**). The metal–metal distances are Pt–Os(1) 2.624, Pt–Os(2) 2.805, Pt–Os(2′) 2.901, Os(1)–Os(1′) 2.537, Os(1)–Os(2) 2.831, Os(1)–Os(2′) 2.807, Os(1)–Os(3) 2.872, Os(1)–Os(3′) 2.768, Os(2)–Os(2′) 2.708, Os(3)–Os(3′) 2.647. All distances are in Å with 0.001 Å e.s.d's.

The cluster (**2**) is a 108 electron system although it has the same metal core geometry as the osmium anion $[HOs_8(CO)_{22}]^-$, which is a 110 electron system.[11] The structure of $[HOs_8(CO)_{22}]^-$ could not be predicted by conventional skeletal electron counting procedures[8] but it can be rationalized by the condensed polyhedra approach.[8] Neither the two aforementioned methods nor the topological electron counting scheme[12] is in agreement with the structure of (**2**). The unusual structure of $[HOs_8(CO)_{22}]^-$, compared to the isoelectronic cluster $[Os_8(CO)_{22}]^{2-}$, was argued on the basis that the presence of hydrogen ligands stabilizes different geometries.[11] If (**2**) was reformulated as a dihydride it would

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† *Crystal data:* $[C_{32}H_{24}Pt_2Os_6O_{16}]$, monoclinic, space group $C2/c$, a = 21.178(3), b = 11.683(2), c = 17.383(2) Å, β = 113.8(4)°, Z = 4, U = 3934.1 $Å^3$, D_c = 3.75 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 265.5 cm^{-1}, $I/\sigma(I) > 3.0$, R = 0.0344, for 2679 absorption-corrected reflections. Intensity data were measured ($2\theta_{max.}$ = 45°) *on an* Enraf–*Nonius* CAD4 diffractometer with less than 0.5% decomposition during data collection. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

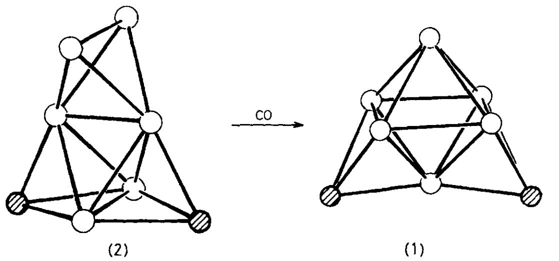

Figure 2. The rearrangement of the metal core of $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$(**2**) to $[Os_6Pt_2(CO)_{17}(C_8H_{12})_2]$(**1**) on reaction with CO. The Pt atoms are shaded.

be isoelectronic with $[HOs_8(CO)_{22}]^-$ and its structure could be explained in a similar manner. There is, however, no marked distortion in the structural parameters of (**2**) which would indicate the presence of a hydride ligand nor could any resonances other than due to the C_8H_{12} protons be located in the ^1H n.m.r. spectrum at 25 or −30 °C. A careful examination of the residual electron density in the crystal structure of (**2**) has not revealed any evidence of another two-electron ligand, and we are confident that the formulation of (**2**) as $[Os_6Pt_2(CO)_{16}(C_8H_{12})_2]$ is correct.

A comparison of the metal–metal distances in (**2**) and $[HOs_8(CO)_{22}]^-$ reveals some interesting differences. The dimensions associated with the bicapped tetrahedron appear normal,[2,11,13] as does the Os(1)–Os(3) distance. Thus capping $Pt(C_8H_{12})$ units do not introduce any major perturbations into the metal core geometry. The edge which is common to both tetrahedra, Os(1)–Os(1′), has a distance of 2.537(1) Å which is the shortest so far reported for an Os cluster compound. The same trend was observed for $[HOs_8(CO)_{22}]^-$ [2.600(1)Å] and this prompted speculation about the possibility of an Os–Os double bond. In (**2**) the Os(3)–Os(3′) distance, 2.647(1) Å, is also very short while the value reported for the corresponding distance in the Os cluster anion $[HOs_8(CO)_{22}]^-$, 2.848(1) Å, is a more typical Os–Os bond length. Although this comparison is somewhat clouded as the hydride is believed to bridge that edge in the Os cluster anion, the Os(3)–Os(3′) distance in (**2**) is unusually short. This short contact is in agreement with an Os(3)–Os(3′) double bond which must be formally assigned to this edge if the metals are to achieve an 18-electron configuration.

The conclusion that (**2**) is a co-ordinately unsaturated cluster is supported by the observed reactivity. Solutions of (**2**) react immediately with carbon monoxide, in CH_2Cl_2 at 23 °C, to give (**1**) in 60% yield (Figure 2). We have been, as yet, unable to grow *X*-ray quality crystals of the only other product formed in this reaction; however this second complex has physical properties which are similar to those of (**1**) and it may be a structural isomer of the bicapped octahedral core.

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